

# PATENT ABSTRACTS OF JAPAN

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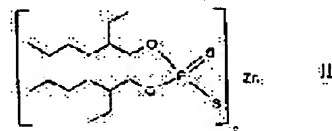
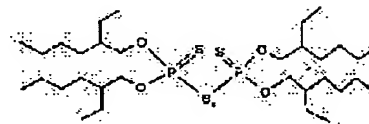
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## (54) REVERSION-FREE VULCANIZATION OF NATURAL AND SYNTHETIC RUBBER USING DITHIOPHOSPHATE AS ACCELERATOR

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a rubber compound vulcanizable without causing reversion by adding a specific polysulfide in combination with a metal alkyl dithiophosphate and/or mercaptobenzothiazole to a rubber.

SOLUTION: (A) A natural rubber and/or a synthetic rubber (e.g. polybutadiene) is compounded with (B) 0.1-10wt.%, preferably 1.5-4wt.% (based on the component A) of a dithiophosphoric acid polysulfide having a 4-12C alkyl group [preferably the compound of the formula I ((x) is 1-10), etc.], (C) 0.5-8wt.%, preferably 2-5wt.% of a metal alkyl dithiophosphate (preferably the compound of the formula II) and/or mercaptobenzothiazole and, as necessary, conventional additives. The compound is vulcanizable usually by heating at <math>\leq 200^{\circ}\text{C}</math> for 1-20min.



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**CLAIMS**

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[Claim(s)]

[Claim 1] They are 0.5 to 8 % of the weight, and the vulcanization nature rubber compound which contains the usual additive arbitrarily including nature and/or synthetic rubber about the alkyl dithio phosphate and/or the mercaptobenzothiazole of 0.1 to 10 % of the weight, and a metal in the dithio phosphoric acid polysulfide in which each \*\*\*\* is calculated on the basis of the amount of rubber, and has C4-C12 alkyl group.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001] If the vulcanization which used sulfur for the rubber which has a carbon-carbon double bond, especially natural rubber is made to be received, reversion (reversion) will be observed, namely, if the optimum value of vulcanization is exceeded, it will be observed that retreat of bridge formation takes place and it will depend on a vulcanization system for the speed to which this happens. If retreat of such bridge formation takes place, aggravation of a mechanical property will be brought about. If a hardening meter examination (cure-meter test) is used, the directions about the influence which heat has on the tensile stress of vulcanized rubber are obtained, therefore the conclusion about the thermal resistance of vulcanized rubber and the conclusion concerning reversion conversely can be pulled out.

[0002] As a result of examining, depending for the inclination of reversion on selection of an accelerator was shown. Many possibility of making reversion into the minimum is, i.e., 1., which may exist. If the amines emitted from an accelerator under the acid addition vulcanization conditions to a rubber compound are made to react with an acid, as long as the salt generated and this salt generation has taken place, the amine which may be considered to be related to reversion is removed.

[0003] 2. the selection doubled with the purpose of a vulcanization accelerator which gives very low reversion -- and combine and the examples of such an accelerator are a mercaptobenzothiazole and a dithio zinc phosphate. However, it is said that it is usable only in the combination of the further accelerator, for example, sulfenamide etc., to use both independently impossible because the rate of vulcanization which will be obtained if it does not do so is not enough. It is not lost although reversion will fall if these two accelerators are combined.

[0004] 3. use of "the matter for restoration" -- mean that such matter restores the network structure partially destroyed at the reversion reaction. About this mechanism, nothing is essentially understood. The effect observed is quite small.

[0005] 4. replacing sulphuric [ some of ] by the sulfur donator -- although it means that this makes high the degree from which the bridge formation (it is thought that stability improves by this) by the oligo-sulfide takes place instead of bridge formation by the poly-sulfide, the dynamic intensity of the vulcanized rubber obtained by doing in this way gets worse. Furthermore, if a commercial sulfur donator is used, an amine dissociation product will be brought about during vulcanization, this may cause reversion, therefore an effect is negated.

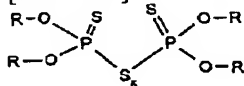
[0006] this invention carries out vulcanization of nature and synthetic rubber based on realization-izing in a format without reversion by using the vulcanization system containing the alkyl dithio phosphate and/or the mercaptobenzothiazole of a dithio phosphoric acid polysulfide and a metal which have C4-C12 alkyl group.

[0007] Therefore, this invention offers a vulcanization nature rubber compound, and includes [ the dithio phosphoric acid polysulfide which calculates each \*\*\*\* on the basis of the amount of rubber, and has C4-C12 alkyl group ] the usual additive for metalead alkyl dithio phosphate and/or a metalead mercaptobenzothiazole in this compound 0.1 to 10% of the weight here at 0.5 to 8 % of the weight, and arbitration including nature and/or synthetic rubber.

[0008] The examples of the rubber according to this invention are the copolymers of the copolymers of natural rubber and synthetic rubber, for example, a polybutadiene, a butadiene / styrene, and a nitrile rubber, for example, a butadiene/acrylonitrile.

[0009] The dithio phosphoric acid polysulfides which have suitable C4-C12 alkyl group are formulas. [0010]

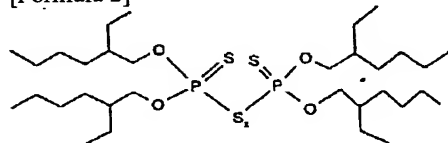
## [Formula 1]



[0011] It is equivalent to [10] from the inside of a formula, R=C4-C12 alkyl, and x= 1.

[0012] The example of a suitable typical compound. [0013]

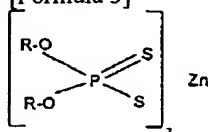
## [Formula 2]



[0014] It comes out, and it is and is x= 1 to 10 here.

[0015] Setting within the limits of the meaning of this invention, metaled alkyl dithio phosphate is a formula. [0016]

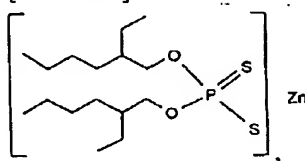
[Formula 3]



[0017] It is the compound expressed with [the inside of a formula, and R=C4-C12 alkyl].

[0018] The example of a suitable typical compound. [0019]

[Formula 4]



[0020] It comes out.

[0021] It calculates on the basis of rubber, and dithio phosphoric acid polysulfides are especially used in 1.5 to 4% of the weight of an amount suitably 9% of the weight from 1.0. It calculates on the basis of rubber, and metaled alkyl dithio phosphate and/or metaled mercaptobenzothiazoles are especially used in 2 to 5% of the weight of an amount suitably 7% of the weight from 1. The quantitative ratio of the dithio phosphoric acid polysulfide to metaled alkyl dithio phosphate and/or a metaled mercaptobenzothiazole is suitably set to 0.5 from 0.25.

[0022] The operation during 1 to 20 minutes at the temperature of 200 degrees C or less is usually possible for vulcanization of the rubber compound according to this invention in a format.

[0023]

[Example]

Vulcanization is made to be received the same time by both (150 degrees C and 180 degrees C), preparing an example 1 rubber compound and eliminating air. A compound and the obtained result are shown in Table 1. The amount shown about the matter is the weight section.

[0024] The sulfur donator which can dissociate amines under the usual vulcanization conditions is compared with the sulfur donator according to this invention. During the vulcanization using sulfur, it is the purpose which eliminates the influence (this is described by reference and is actually observed) the sulfur structure of cross linkage is influenced, and the vulcanization system which does not contain free sulfur is chosen.

[0025] Tensile stress 300 is suitable directions of reversion. Although it was shown by the sulfur donator (A2, B1, C3) which can dissociate an amine that tensile stress 300 declines 50% from 40 when 30 degrees C of temperature to heat were made high, the sulfur donator (D5) according to this invention does not show change of tensile stress 300 at all. Although it is only 30% when an alkyl dithio zinc phosphate is transposed to the iso octyl amine salt of dithio phosphoric acid, tensile stress 300 declines (F6). This means that it is not so good even if reversion takes to make it not happen notably and uses as an amine salt amines (this is dissociated from the sulfur donator used by A2, B1, and C3 as known). Therefore, reversion is not enough to make it not happen though such amines are caught from an acid, for example, stearin acid etc.

[0026] Heat aging and a mechanical test are combined and a compression set is measured by making the force act on a sample at an elevated temperature. The compression set measured at various temperature is comparison between the sample in which vulcanization was made to be received at 180 degrees C, and the sample in which vulcanization was made to be received at 150 degrees C. When the sulfur donator according to this invention is used (here) If a compression set value makes bridge formation being improved 3% received from 15 by contrast using a JICHIOJI morpholine (DTDM) (A2) if about 60 to 30% of R/C is shown according to a test temperature and test time and bridge formation is made to be received using a dithio caprolactam (DTDC) (B1, C3) -- the R/C -- 20 to 10% -- becoming -- and . If a dithio zinc phosphate is transposed to the amine salt of dithio phosphoric acid (F6), the sinking rate of a compression set value will become 10 to 0%.

[0027] Comparison of examinations D5 and F6 shows that tensile stress 300 declines notably as it will make a curing temperature high, if a dithio zinc phosphate is transposed to a dithio phosphoric acid amine salt. So, in making a salt generate, it came to a conclusion to repeal completely negative influence which amines show, when impossible.

[0028]

[Table 1]

表1

試験	A2		B1		C3		D5		F6	
天然ゴム	100		100		100		100		100	
カーボンブラック	35		35		35		35		35	
酸化亜鉛	5		5		5		5		5	
ステアリン酸	1		1		1		1		1	
ジチオジモルホリン	2		-		-		-		-	
ジチオカプロラクタム	-		3		3		-		-	
ビス(0,0-2-エチル ヘキシルチオホスホリル) ポリスルフィド	-		-		-		5.8		5.8	
ジ-イ-オクチル- ジチオ炭酸亜鉛	1		1		-		1		-	
ジ-イ-オクチル- ジチオ炭酸アミン塩	-		-		1		-		1	
加硫時間(分)	23		18		18		12		12	
加硫温度(℃)	150	180	150	180	150	180	150	180	150	180
硬度(°ショアA)	40	36	43	38	42	39	45	45	45	45
弾性(%)	36	36	37	37	36	35	35	38	35	39
引張り応力100(MPa)	1.0	0.7	1.3	0.8	1.3	0.8	1.4	1.3	1.4	1.2
引張り応力300(MPa)	5.1	3	6.3	3.2	6.7	3.2	7	7	7.2	5.8
無限引張り強度 (MPa)	16	8	19	10	20	10	22	18	22	18
破断伸び(%)	550	343	550	555	550	360	565	515	560	360
圧縮永久歪み(%)	194									
24時/70℃	30	49	36	43	32	47	29	25	29	27
24時/90℃	33	62	35	52	49	54	42	37	43	39
72時/90℃	37	73	60	65	56	65	34	31	33	33

[0029] The vulcanization system which includes free sulfur as an additional component to an example 2 sulfur donator is chosen. the \*\*\*\* standard vulcanization system which usually boils the selected comparison system in this field, and is used -- it is -- this system -- a good shell -- it makes it possible to manufacture the vulcanized rubber which shows good physical properties and an aging property very much (5E) The result is shown in Table 2.

[0030] Respectively, when each \*\*\*\* is made into the same curing time with the vulcanization in 150 degrees C, and the vulcanization in 180 degrees C, the degree to which tensile stress 100 declines in comparison compound 5E is notably larger than the case of Examinations 6B, 6C, and 6E.

[0031] When temperature which heats vulcanized rubber is made high and it is Examinations 6E, 6C, and 6B although the compression set of a comparison compound got worse 17%, it points out that 8-10% improvement was carried out.

[0032] If it follows on making heating temperature high and a network structure becomes stability more, it should assume, therefore this shows that reorientation seldom happens under a compression set test condition, and on the other hand, by examination 5E, if heating temperature is made high, a network structure will become unstable.

[0033] As for this, hot blast aging also appears again. While the inclination softened although the degree of hardness in examination 5E does not change in essence is shown, by Examinations 6E, 6C, and 6B, the Shore A degree of hardness rises by about 8 degrees on an average. It becomes possible to oppose such an inclination for a suitable amine to happen by being added as an impurity.

[0034]

[Table 2]

表 2

試験	5E		6E		6C		6D	
天然ゴム	100		100		100		100	
カーボンブラック	50		50		50		50	
ナフテン系石油	5		5		5		5	
酸化亜鉛	5		5		5		5	
ステアリン酸 (重量部)	1		1		1		1	
S-80 (硫黄 80%)	0.5		0.5		0.5		0.5	
TBBS-80	0.8		-		-		-	
OTOS	1.2		-		-		-	
SDT-70	-		9		9		9	
ZDODP-70	-		1		0.5		-	
MBTS-80	-		-		0.5		1	
加硫時間 (分)	13		16		18		18	
加硫温度 (°C)	150	180	150	180	150	180	150	180
硬度 (°ショア A)	61	56	56	54	60	58	62	61
弾性 (%)	63	61	63	59	67	64	67	65
引張り応力 100 (MPa)	3.8	2.6	3.3	2.2	3.6	3.6	4.3	3.6
引張り応力 500 (MPa)	15.8	8.1	17	7.8	17.8	16.8	17.9	14.4
極限引張り強度 (MPa)	20	19	19	18	18	19	19	18
破壊伸び (%)	315	355	350	400	305	320	295	305
圧縮永久歪み (%)								
24時/90℃	17	36	26	16	20	12	19	11
24時/100℃	27	32	32	29	29	22	30	21
24時/125℃	42	59	42	32	38	30	37	29

[0035] TBBS=N-t-butyl-2-benzothiazyl sulfenamide OTOS=N-oxy-diethylene dithio carbamyl-N-oxy-diethylene sulfenamide  
SDT= screw (0 and 0-2-ethylhexyl thio HOSUHORIRU) polysulfide ZDODP= G soak chill dithio zinc-phosphate MBTS=  
dibenzothiazyl disulfide

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